

SCORCH PREVENTION IN FLEXIBLE

POLYURETHANE FOAMS

Field of the Invention

5 The present invention relates to the prevention of discoloration in flexible polyurethane foams, a phenomenon commonly referred to as "scorching". More particularly, the invention relates to novel compositions useful to alleviate or prevent the aforementioned undesirable effect.

Background of the Invention

Scorching is an undesirable discoloration phenomenon which occurs within polyurethane (PU) foam blocks, causing them to assume a yellow to brown color. This discoloration is especially apparent in the center of the blocks where the internal temperatures remain high for a relatively long period of time. The exposure of the interior of the foams to high
15 temperatures leads to embrittlement and the core discoloration commonly known as scorching. In extreme cases this can result in ignition of the foam buns, sometimes with disastrous consequences. In some severe cases, it can cause a degradation of physical properties or, where scorching is particularly intense, can result in spontaneous combustion of freshly made foam blocks.

20 Flame retardants (FR), with few exceptions, exacerbate the "scorch" problems that arise during processing of PU foams. Flame retardants create several problems for the manufacturers of water-blown, flexible, slab stock foams, including increased "scorch" during processing and increased smoldering tendency of foams subjected the California
25 TB 117 standard.

Antioxidants have been proposed for use in flame retarded foams, but by themselves they are not very efficient. For example when halogen containing FR are present in the formulation. The art has so far failed to provide a generally efficient solution to the
30 problem of scorch taking place during the manufacturing of flexible polyurethane foams comprising any FR selected from those used in the art.

It is therefore an object of the present invention to provide an anti-scorch composition addressing the problem of scorch for flame-retarded flexible polyurethane formulations.

It is another object of the present invention to provide an anti-scorch composition that efficiently addresses the problem of scorch for flexible polyurethane formulations flame retarded with scorch-inducing FR such as phosphorus-based FR or halogen-containing FR, whether aliphatic or aromatic halogenated FR, or their combination.

It is still another object of the invention to provide an anti-scorch combination that overcomes the drawbacks of the prior art.

It is yet another object of the invention to provide a method for preventing or diminishing the occurrence of scorch during the manufacturing of flexible polyurethane foams.

Other purposes and advantages of the invention will become apparent as the description proceeds.

Summary of the Invention

The invention provides an anti-scorch composition for flame-retarded flexible polyurethane foams, comprising at least one antioxidant agent, an epoxy compound, and at least one organic phosphite alone or in combination with at least one metal salt of a monocarboxylic or dicarboxylic acid. Said organic acid is selected from among saturated or unsaturated, aliphatic or aromatic, and monocarboxylic or dicarboxylic organic acids. Said metal salt is selected from the group consisting of salts of Ca, Zn, Ba, and Sn. An illustrative example of such salts may include barium oleate, barium t-butylbenzoate, barium ethylhexanoate, zinc t-butylbenzoate, calcium dimethyl ethylbenzoate, etc. Said at least one antioxidant agent, i.e. one or more compounds, may be selected from among phenols and amino oxygen scavengers, and their mixtures. Said phenol is preferably a hindered phenol, and said amino oxygen scavenger is preferably an alkylated diphenylamine. In a preferred embodiment of the invention, said at least one antioxidant agent comprises a mixture of hindered phenol and an alkylated diphenylamine. The flame-retarded foams of the invention may be retarded by any FR known in the art. In a

preferred embodiment of the invention, the PU foams are retarded with phosphorus-based flame retardant (FR). In another embodiment, said flame-retarded foams are retarded with a halogen-containing flame retardant, e.g. with an aliphatic or aromatic brominated or chlorinated FR. Non-limiting examples of FR possibly used in the composition of the invention include brominated epoxy, tribromoneopentyl alcohol, tris(2-chloroisopropyl) phosphate, chlorinated alkylphosphate ester, halogenated aryl esters/aromatic phosphate blend, and pentabromobenzyl alkyl ethers. The composition with reduced scorch phenomenon according to this invention comprises an epoxy compound, which may be, for example, selected from among diglycidyl ether of bisphenol A and its derivatives. Said epoxy compound, added to the mixture of the invention, has available epoxy groups, i.e., epoxy groups essentially not neutralized by previous curing. Said organic phosphite may be, for example, selected from among tris(alkylphenyl) phosphites, trialkyl phosphites, dialkyl phenyl phosphites, alkyl diphenyl phosphites, and triphenyl phosphites.

The invention further provides a method for preventing or diminishing scorch in a flame-retarded flexible polyurethane foam, comprising adding to the polyurethane composition, prior to foaming, at least one antioxidant agent, an epoxy compound, and an organic phosphite alone or with at least one metal salt of a monocarboxylic or dicarboxylic acid. Illustrative and non-limitative examples of antioxidant agents are phenols and amino oxygen scavengers, such as hindered phenols. Illustrative and non-limitative examples of amino oxygen scavengers include alkylated diphenylamines. The flame-retardant may be a phosphorus-based flame retardant, and/or halogen-containing flame retardant, e.g. an aliphatic or aromatic brominated or chlorinated FR. According to a further preferred embodiment of the invention the composition further comprises an epoxy compound, such as – but not limited to – diglycidyl ether of bisphenol A and its derivatives.

The above and other objects and advantages of the invention will be better understood from the following illustrative and non-limitative examples.

Examples 1-15

Microwave (MW) test protocol for scorch evaluation

The test method consists of the following steps:

1. Foam production in a small shoe box with a square cross-section.
2. Immediately after the foam rise is complete (usually less than 2 minutes), the foam is heated using a microwave (MW) oven using a predetermined time and power level.
3. The foam is then heated in an oven at $120 \pm 2^\circ\text{C}$ for 2 min.
- 5 4. The foam is allowed to cure at RT (room temperature) for an additional 15 min.
5. By the end of the RT curing time the foam is cut (usually vertically) and the scorch is observed.

Scorch evaluation

10 The scorch is evaluated using two methods:

1. The foam is photographed using a digital camera. This allows for a visual comparison between the scorch of a reference formulation and the scorch of the formulation under investigation.
2. The foam color is analyzed using a spectrophotometer. The results are expressed in the
15 usual color space: L^*a^*b and performed accordingly to ASTM D-2244.

Note: The scorch intensity may change from day to day according to the physical conditions of the surroundings in which the foam has been prepared (usually the temperature and relative humidity). This is why it is customary to prepare each day a reference sample.

20

Foam preparation

The mixture was prepared in a 0.65 l disposable cup. The components were added one at a time starting with the polyol. The mixture was vigorously mixed at 3500 rpm for 10 seconds following the addition of each component, not including the Toluene diisocyanate
25 (TDI). After the addition of TDI, the mixture was mixed for an additional 10 sec and then poured into a 25X25X17 cm cardboard box. The times between the TDI addition and the pouring into the cardboard box and the end of the foam blowing (rise time) were monitored.

Comparative samples and results

30 The effect of the antiscorching ingredients and their combinations was measured on the darkest areas on the foam after microwave oven treatment, using a spectrophotometer

which provides color measurements expressed in the L*a*b color space. The most relevant color parameters for scorch assessment are Δb and ΔE .

The color parameters are given as normalized values relative to the reference specimens.

- 5 As explained in the MW oven procedure, this particular method for scorch propensity assessment requires that a new reference foam be prepared, subjected to MW oven procedure and measured in each and every day of measurements. This requirement is related to the effect various experimental conditions, such as the temperature and the relative humidity of the air in the lab may have on the level of scorch. The normalized Δb and ΔE differences between a reference foam (containing no antiscorching ingredients)
- 10 and foams containing various ingredients with antiscorch effects, are calculated as follows:

$$\Delta\Delta b(\text{normalized}) = \frac{\Delta b(\text{reference}) - \Delta b(\text{sample})}{\Delta b(\text{reference})} \bullet 100$$

$$\Delta\Delta E(\text{normalized}) = \frac{\Delta E(\text{reference}) - \Delta E(\text{sample})}{\Delta E(\text{reference})} \bullet 100$$

15

Note: A value greater than 100 can sometimes emerge from these calculations since both Δb and ΔE for each specimen are compared to a factory white standard. The higher the $\Delta\Delta b$ and $\Delta\Delta E$ values, the lower the scorch.

- 20 Formulations for two grades of foams are shown in Tables I and II: Medium density foams (Table I) have a density of approximately 25 Kg/m³; Low density foams (Table II) have a density of approximately 15 Kg/m³. The component amounts in tables I, II, IV, and V are expressed as weight parts relative to 100 parts of polyol (phr).

- 25 Ingredients: AO1 and AO5 are antioxidants produced by Goldschmidt (Degussa) and contain combinations of hindered phenols and aromatic diamines.

Epoxy 828 is Diglycidyl ether of bisphenol A (DGEBA).

ESBO = Epoxidized Soya Bean oil.

All other ingredients below the FR-513 line in the table are metallic salts (Ca, Zn, Ba, Sn)

- 30 of organic acids, and organic phosphites.

Table I Anti-scorch performance of medium density foams

	1	2	3	4	5	6	7	8	9
Polyol	100	100	100	100	100	100	100	100	100
Water	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
Silicon 8228	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Amine Dabco 33LV	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Amine BDE	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Tin T-9	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Toluene di-isocyanate (TDI)	56.31	56.31	56.31	56.31	56.31	56.31	56.31	56.31	56.31
FR-513	5	5	5	5	5	5	5	5	5
AO5	0.42	0.21	0.85						
Calcium stearate (CaSt)	0.42	0.21							
PK4610	0.42	0.21							
Epoxy 828			0.85		0.1	0.1	0.21		
ESBO				1.7					
LZB 138					0.21			0.21	0.21
AO 1					0.21	0.21	0.21	0.21	0.21
CZ400						0.21		0.21	
CZ 118 S							0.21		0.21
$\Delta\Delta b$	90.13	106.1	49.17	-132.6	82.32	77.06	93.93	84.58	102.9
$\Delta\Delta E$	17.04	10.84	18.34	-99.43	27.61	32.67	30.14	37.42	33.98

Table II Anti-scorch performance of low density foams

	10	11	12	13	14	15
Polyol	100	100	100	100	100	100
Water	5.25	5.25	5.25	5.25	5.25	5.25
Silicon 8228	1.0	1.0	1.0	1.0	1.0	1.0
Amine Dabco 33LV	0.06	0.06	0.06	0.06	0.06	0.06
Amine BDE	0.046	0.046	0.046	0.046	0.046	0.046
Tin T-9	0.37	0.37	0.37	0.37	0.37	0.37
Methylene Chloride (MeCl)	11	11	11	11	11	11
TDI	71.1	71.1	71.1	71.1	71.1	71.1
FR-513	15	15	15	15	15	15
AO5			0.1	0.3		0.2
Epoxy 828	0.5	1.0				
BM270					1.0	0.2
LZB287						0.6
$\Delta\Delta b$	-14.11	24.37	-15.10	-77.1	95.29	50.90
$\Delta\Delta E$	0	13.73	-10.13	-41.03	27.80	11.70

Table III Composition of ingredients used as antiscorch materials.

Producer	Name	Ingredients		State
Akeros	Lankromark LZB287	1) Barium oleate Barium t-butylbenzoate	40%	Liquid
		2) Zinc 2-ethylhexanoate	5-10%	
		3) Phosphite esters	20-40%	
		4) 2-(2-butoxyethoxy)ethanol	5-10%	
		5) Phenol	5-10%	
	Lankromark LZB413	1) Barium 2-ethylhexanoate Barium oleate Barium t-butylbenzoate	20%	Liquid
		2) Zinc 2-ethylhexanoate	1-5%	
		3) Zinc t-butylbenzoate	1-5%	
		4) Phosphite esters	20-40%	
		5) Tris(nonylphenyl) phosphite	1-5%	
		6) 2-(2-butoxyethoxy ethanol)		
	Lankromark LZB138	1) Barium oleate Barium t-butylbenzoate	~30%	Liquid
		2) Zinc 2-ethylhexanoate	10-20%	
		3) Phosphite esters	20-40%	
		4) 2-(2-butoxyethoxy) ethanol	5-10%	
		5) Phenol	1-5%	
	Lankroflex E2307	1) Epoxidized soya bean oil	> 99%	Liquid
	Tinstab BTS71S	1) n-Butyltin tris (2-ethylhexylthio-glycolate)	~20 %	Liquid
		2) Di-n-butyltin bis (2-ethylhexylthio-glycolate)	~70%	
	Tinstab BM270	1) Di-n-butyltin bis (methylmaleate)	~95%	Liquid
Shell	Epoxy 828		~100%	Liquid
Chemson Group	Naftosafe PK4610	Ca/Zn organic stabilizer	-	Powder
Gold-schmidt	Ortegol AO1	Steric hindered phenol derivate	66.7%	
		Alkylated diphenylamine	33.3%	
	Ortegol AO5	Steric hindered phenol derivate	70-72%	
		Alkylated diphenylamine	20-22%	
	Mark CZ 400 (Ca/Zn stabilizer)	2-(2-Butoxyethoxy)ethanol	<10%	Liquid
		Alkylarylphosphites	55-65%	
		Calcium 4-(1,1-dimethylethyl)benzoate	<10%	
		Tris(nonylphenyl)phosphite	30-40%	

Crompton	Mark CZ 118S (Ca/Zn stabilizer)	Other components - not listed		Liquid
	Mark BZ 592 (Ba/Zn stabilizer)	Solvent naphta, light aromatic	<10%	Liquid
		Barium compounds	35-45%	
		Triisodecyl phosphite	<25%	

Producer	Name	Ingredients		State
Crompton	Mark BZ 562 (Ba/Zn stabilizer)	Solvent naphta, light aromatic	<10%	Liquid
		Alkylarylphosphites	20-30%	
		Zinc bis(p-nonylphenolate)	<3%	
		Barium compounds	35-45%	
	Mark BZ 555 (Ba/Zn stabilizer)	Tris(2-ethylhexylmercaptoacetate) phosphate	5-15%	Liquid
		Diisodecyl phenyl phosphite	25-35%	
		Solvent naphta, light aromatic	5-15%	
		Barium compounds	20-30%	
	Mark BZ 563 (Ba/Zn stabilizer)	Diisodecyl phenyl phosphite	30-50%	Liquid
		2-(2-Butoxyethoxy)ethanol	<5%	
		Zinc bis(p-nonylphenolate)	<5%	
		Barium compounds	20-30%	

From the results in Tables I and II it is clearly seen that the compositions of the invention
5 attain a substantial improvement.

The notations and composition of materials used as antiscorch ingredients in the examples
in Tables I and II are detailed in Table III.

10 Example 3 in Table I and Examples 12 and 13 in Table II, respectively, demonstrate that
the use of a conventional antioxidant, i.e. a mixture of hindered phenols and alkylated
diphenyldiamines, alone or together with an epoxy moiety, does not prevent scorch in a
bromine-containing FR formulation. Epoxy alone, either as DGEBA or ESBO, are not
effective either (Examples 4 in Table 1, and Examples 10 and 11 in Table II). However,
15 addition of organic phosphites alone or in combination with metallic salts of various

organic acids, significantly improves the resistance to scorch of a polyurethane flexible foam formulation including a bromine-containing flame retardant (Examples 8, 9 - Table I, and Examples 14, 15 - Table II).

5

Examples 16-25

MW test protocol for scorch evaluation

1. Foam production in a small shoe box with a square cross-section.
2. Immediately after the foam rise is complete (usually less than 2 minutes), the foam is
10 heated in a microwave (MW) oven that is equipped with an electronic controlling circuit that controls the overall heating energy emitted by the MW oven. Controlling feedback is accomplished via measuring the temperature of a given constant mass of water co-heated alongside the foam. The water temperature closely follows a pre-set rate of temperature rise (ramp) over a predetermined period of time so that a constant temperature difference
15 is maintained in each heating cycle.
3. The foam is then placed in an oven at 110-120°C for 17 minutes not only to cure but also to slow down the foam's natural cooling and to isolate it from climate and surrounding changes as well. The foam's core temperature is being monitored throughout this stage with a k-type 1.6 mm diameter thermocouple plugged into a data-logger.
- 20 4. Following the 17 minutes curing the foam is sliced perpendicular to foam rise direction, obtaining square cross-section slices. The surface of the central slice is then photographed and its scorch level is evaluated.

Digital scorch evaluation

- 25 The effect of anti-scorching ingredients on various scorch-forming halogenated flame retardants in various common flexible polyurethane formulations was measured all over the surface of the central foam slice, where the foam core temperature was the highest along the disclosed procedure, rather than locally on selected darkest zones alone. Digital photographs taken under fully controlled parameters (illumination, filming angles) were
30 processed by graphic software that scans the photographs having the same resolution and sums up the number of pixels having different colors over a selected slice area. The resulting value, Unique Colors (UC), highly correlates with the visual comparative

inspection of scorch intensity. The UC values are straightforward, the lower they are the less scorched is the foam. A reduced UC value indicates a better anti-scorch effect.

Note: the controlled emission of the MW energy during the foam heating stage of the test procedure, together with the controlled and slowed down cooling of the foam that is isolated from the surrounding climate changes, were statistically proved to accomplish highly reproducible day-to-day results. Scanning to measure the entire scorched area also was well contributing to the accuracy and reproducibility of the test procedure. Nevertheless, often a reference formulation was carried as an internal test to assure that test parameters are fully kept and the resulting scorch intensity falls within the narrow variability limits of the procedure.

Foam preparation

The foam mixture was prepared in a 0.65 l disposable cup. All components, but the water and the toluene di-isocyanate (TDI), were successively added starting with the polyol. The mixture was vigorously mixed at 4400 rpm for 15 seconds, followed by the injection of pre-weighed water under continuous mixing. Mixing was allowed for 20 seconds more before the pre-weighed TDI was introduced, followed by 10 seconds of further mixing and an immediate pouring of the mixture into a 25x25x17 cm³ cardboard box. Foam rise time, from pouring to blow-off, was recorded.

Various halogen-containing common commercial flame retardants, among them some well known to be accompanied by an intense scorching process, were introduced into the foam formulations. The marked effect of the combination of the anti-scorching components was demonstrated by comparing the measured scorch intensity (UC values) with and without the presence of each of these flame retardants in the formulation. These results and the normal density formulation (foam density ca. 25 Kg/m³ in FR-513 containing foams) used with the various flame retardants - with the necessary changes of TDI - is presented in table IV. The efficacy of the same combination of anti-scorching components toward various halogen-containing flame retardants is shown to be equally high for different foam formulations or foam densities, as presented in table V.

A combination of anti-scorch ingredients according to the invention, comprising hindered phenol, alkylated diphenylamine, epoxy compound, and organic phosphites with or without metallic salts of organic acids, is demonstrated hereafter to effectively diminish or prevent the scorch occurrence within foams containing scorch-forming flame retardants, such as: halogenated - wherein the halogen is either aromatic or aliphatic - and/or halogenated phosphates - wherein the halogen is either aromatic or aliphatic- and/or phosphorus-based flame retardants. Illustrative and non-limitative examples of such flame retardants are: tribromoneopentyl alcohol (FR-513 ex Dead Sea Bromine Group, DSBG), tris(2-chloroisopropyl) phosphate (TCPP, Fyrol FR-2 ex Akzo Nobel), chlorinated alkylphosphate ester (Amgard V6 ex Albright and Wilson/ Antiblaze V6 ex Albemarle), Halogenated aryl esters/Aromatic phosphate Blend (FM-550 ex Great Lakes), pentabromobenzyl alkyl ethers (FR-1435X ex DSBG), brominated epoxy F-3014 (ex DSBG) dissolved in phosphates (Phosflex 31L ex Akzo Nobel) 1:1 w/w.

- The selected combination of the anti-scorch ingredients comprises the materials:
- AO5: Antioxidant produced by Goldschmidt (Degussa), containing a combination of hindered phenols and aromatic diamines.
- Epoxy 828: EPONTM Resin 828 produced by Resolution Performance Products is Diglycidyl ether of bisphenol A (DGEBA).
- Metallic (Ba, Zn, Ca or Sn) salts of organic acids and organic phosphites are included in BaerlocherTM product.

Table IV Anti-scorch performance of medium density foams with halogenated or phospho-halogenated flame retardants

Ingredient	16	16a	17	17a	18	18a	19	19a	19b	20	20a	21	21a
Flame retardant	Fyrol FR-2 (TCPP)		Amgard V6 (Antiblaze V6)		F-3014 & Phosphates		FR-513			FM 550		FR-1435X	
	15		10		13		8			14		14	
Polyol	100		100		100		100			100		100	
Silicon Nix L-650	0.95		0.95		0.95		0.95			0.95		0.95	

Amine Dabco 33LV	0.018		0.018		0.018		0.018			0.018		0.018	
Amine BDE	0.0624		0.0624		0.0624		0.0624			0.0624		0.0624	
Tin T-9	0.153		0.153		0.153		0.153			0.153		0.153	
Water	4.63		4.63		4.63		4.63			4.63		4.63	
Toluene di-isocyanate (Index 119)	62.03		62.03		62.53		64.59			62.03		62.03	
Anti-scorch Combinat.1 ^a	0.0	1.0	0.0	1.0	0.0	1.0	0.0	1.0	-	0.0	1.0	0.0	1.0
Anti-scorch Combinat.2 ^b									1.0				
Scorch level (UC)	23408	4927	43188	7777	28238	6134	27414	5640	5238	7111	5950	7806	5956
Scorch reduction, %		-79		-82		-78		-79	-81		-16		-24

^a A combination of anti-scorch components that contains an anti-oxidant, epoxy, organic phosphites and metal salts of organic acids.

^b A combination of anti-scorch components that contains an anti-oxidant, epoxy and organic phosphites.

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The anti-scorch combination (AS package) demonstrated in Table IV is shown to maintain its high efficacy in diminishing or preventing scorching in foams containing scorch-forming flame retardants independently of the foam formulation, or the foam densities (e.g. normal – ca. 25 kg/m³ or low – ca. 15 kg/m³, in FR-513 containing foams).

10 These results are presented in table V.

15 **Table V** Anti-scorch performance of medium and low density formulations with different FRs

Ingredient	22	22a	23	23a	24	24a	25	25a
	Normal density foams - Second formulation				Low density foams			
Flame retardant	Fyrol FR-2 (TCPP)		FR-513		Fyrol FR-2 (TCPP)		FR-513	
	15		6.5		15		8	
Polyol	100		100		100		100	
Silicon Nix L-650	1.1		1.1		1.0		1.0	

Amine Dabco 33LV	0.09		0.09		0.06		0.06	
Amine BDE	0.03		0.03		0.047		0.047	
Tin T-9	0.25		0.25		0.37		0.37	
MeCl ₂	-		-		11.0		11.0	
Water	4.20		4.20		5.25		5.25	
Toluene di-isocyanate (Index 114)	54.68		56.67		66.27		68.72	
Anti-scorch Combinat. 1 ^a	0.0	1.0	0.0	0.81	0.0	1.0	0.0	1.0
Scorch level (UC)	24537	4758	23667	5706	8159	5421	7910	4700
Scorch reduction, %		-81		-76		-34		-41

^a A combination of anti-scorch components that contains an anti-oxidant, epoxy, organic phosphites and metal salts of organic acids.

Considering the background color measured over non-scorched areas, the selected anti-scorch package has been proved to significantly reduce and nearly to diminish scorch occurrence in flexible polyurethane foams containing scorch-forming flame retardants, independently of their formulation or density.

A clear improvement was also achieved in foams containing flame retardant that so far were considered by foam producers to produce an acceptable scorch level, such as the case of FM 550.

All the above description has been provided for the purpose of illustration, and is not intended to limit the invention in any way. Various modifications can be carried out in the method and system according to the invention, without departing from its spirit.